B5

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 4 :
C04B 28/04, 24/12
// (C04B 28/04, 18:08, 24:08
C04B 24:16, 24:32)
(C04B 28/04, 18:08, 24:12
C04B 24:16, 24:32)
(C04B 28/04, 18:08, 24:08
C04B 24:12, 24:16)

A1

(11) International Publication Number: WO 85/01500

(43) International Publication Date: 11 April 1985 (11.04.85)

(21) International Application Number: PCT/US84/01292

(22) International Filing Date: 15 August 1984 (15.08.84)

(31) Priority Application Number: 537,186

(32) Priority Date: 29 September 1983 (29.09.83)

(33) Priority Country: US

(71) Applicant: MARTIN MARIETTA CORPORATION [US/US]; 6801 Rockledge Drive, Bethesda, MD 20817 (US).

(72) Inventor: NICHOLSON, Richard ; 4868 Westbourne Road, Lyndhurst, OH 44124 (US).

(74) Agents: MYLIUS, Herbert, W. et al.; Martin Marietta Corporation, 6801 Rockledge Drive, Bethesda, MD 20817 (US).

(81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), DK, FI, FR (European patent), GB (European patent), LU (European patent), NL (European patent), SE (European patent).

Published
With international search report.

(54) Title: ADDITIVE FOR HYDRAULIC CEMENT MIXES

(57) Abstract

A hydraulic cement mix including hydraulic cement, aggregate, sufficient water to effect hydraulic setting of the cement, and an additive comprising mixtures of alkali and alkanolamine salts of alkylarylsulfonic acids and alpha olefinsulfonic acids, and alkali and alkanolamine salts of fatty acids, and a nonionic components selected from polyethylene glycol derivatires and diethanolamine adducts of cocamide, the mixtures being added at a dosage required to entrain in said hydraulic cement mix a desired level of air, which remains substantially stable on extended mixing.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GA	Gabon	MR	Mauritania
AU	Australia	GB	United Kingdom	MW	Malawi
BB	Barbados	HU	Hungary	NL	Netherlands
BE	Belgium	IT	Italy	NO	Norway
BG	Bulgaria	JP	Japan	RO	Romania
BR	Brazil	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	LI	Liechtenstein	SN	Senegal
CH	Switzerland	LK	Sri Lanka	SU	Soviet Union
CM	Cameroon	LU	Luxembourg	TD	Chad
DE	Germany, Federal Republic of	MC	Monaco	TG	Togo
DK	Denmark	MG	Madagascar	US	United States of America
FI	Finland	ML	Mali		
FR	France				

ADDITIVE FOR HYDRAULIC CEMENT MIXES

BACKGROUND OF THE INVENTION

This invention relates to additive compositions, otherwise known as air-entraining admixtures, for incorporation in hydraulic cement mixes, such as concretes and mortars, but not limited thereto, for the purpose of increasing the durability of such mixes, after hardening, to cycles of freezing and thawing under conditions of water saturation. The increased durability of the cementitious mix under such conditions is attained by incorporation of a system of air bubbles into the plastic mix in such a way that it will remain in the mix after hardening, and meet the specifications of resistance to freezing and thawing set forth in ASTM designation C 260. This requires that the air void system be an appropriate amount as volume percent of the hardened cementitious mass and that it have bubbles of an appropriate range of sizes and spacing parameters as determined by ASTM designation C 457. In order to attain this condition it is well known in the art to use surface agents to effect the desired air entrainment.

A number of chemical agents to achieve a desirable air entrainment are known in the art and are commercially available. Generally, these are organic chemicals having a surface active functionally at the air-water interface and fall broadly into the classes of soaps and detergents. One of the best known agents of this kind is known in the art as Vinsol resin, and is normally employed as an aqueous alkaline solution which is added to a plastic, cementitious mix, either alone or in combination with other admixtures. In the latter case, the Vinsol resin solution is separately added because of the chemical incompatibility with many other admixtures, due to the fact that the pH and the presence of calcium and various other ions renders insoluble the alkali-neutralized acids comprising Vinsol resin. Thus, Vinsol resin is the sodium soap of specific resin acids derived by solvent extraction from pine stumps. It is also known in the art

SUMMARY OF THE INVENTION

The present invention is an additive composition for incorporation in hydraulic cement mixes, such as normal concretes, mortars and grouts and neat cement mixes, with optional replacement of a portion of the hydraulic cement of said mixes with a corresponding amount of pozzolanic material, and the resulting improved cementitious mixes and process for incorporating the additive composition.

For purposes of this invention the term "hydraulic cement" is intended to mean and to include all cementitious compositions based primarily on silicates capable of being set and hardened by the action of water, such as portland cements, sulfate-resisting cements, blast furnace cements and pozzolanic cements, but the preferred use of the present additive composition is in portland cement mixes and such mixes when a portion of the portland cement has been replaced by fly ash. The term "portland cement" is intended to include all cementitious compositions which have a high content of tricalcium silicate, conforming with the specifications set forth in ASTM designation C-150, and the portland blended cements such as those described in ASTM C-595.

Broadly, the invention comprises a hydraulic cement mix including hydraulic cement, aggregate, sufficient water to effect hydraulic setting of the cement, and an additive comprising a mixture of the soluble alkanolamine and alkali salts of fatty acids plus the soluble alkali and alkanolamine salts of certain sulfonic acids such as alpha olefin sulfonic acids plus a third nonionic component such as the fatty acid amides and polyethylene glycol derivatives as well as selected other components, as more fully described hereafter. While these materials may be added in combination in their normal state to a cementitious mix it is most convenient to add them as a single aqueous solution which may have a desired cosmetic coloring agent and if the water employed is not distilled or "deionized" so as to be essentially free of alkaline earth cations, the necessary amount of a chelating agent for these ions may also be added so as to

maintain the additive components in solution. The sodium salt of nitrilotriacetic acid is one example of such a chelating agent. The effect of the additive to entrain a desirable amount and kind of air void system in a variety of cementitious mixes and particularly in mixes containing fly ash having a relatively high carbon content as indicated by an ignition loss of up to 6% or more by weight of fly ash, when the cementitious system is subjected to prolonged mixing up to the order of one hour, was found to depend optimally on the presence of all three of the components described above, although in certain instances combination of two of the three components may produce desirable effects. Thus, the fatty acid salts of soaps which are known as such in the art under prolonged mixing in a cementitious system require relatively high dosages, entrain air slowly, and have a tendency to gain air with extended mixing. The sulfonic acid salts employed alone in cementitious mixes, on prolonged mixing, tend to progressively lose the air which they first entrain. The polyethylene glycol or other nonionic component may or may not of itself be an air-entraining agent in cementitious mixes. However, the unexpected and nonobvious result obtained by employing these three materials in combination in a cementitious system undergoing extended mixing is to yield with a favorable dosage response an excellent air void system stable in the plastic cementitious system and having a desirable improved size and distribution in the cementitious system after hardening.

It is therefore an object of the present invention to provide improved air-entrained hydraulic cement mixes.

It is another object of this invention to provide improved air-entrained hydraulic cement mixes, including concrete, mortar and grout mixes, neat cement and dry mixes, which include an additive composition that will advantageously entrain an air void system having desired characteristics when said additive is employed over a relatively wide dosage range, or have a superior dosage response relative to functionally similar additives known in the art.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The fatty acid salts of the instant invention may be represented by the following formula:

$$RCOOM$$

where R is an alkyl chain that may be branched or unbranched, saturated or unsaturated, but wherein the number of carbon atoms is in the range from about 12 to about 24, and M is an alkali metal, with sodium or potassium being preferred. Optionally, the fatty acid may be neutralized with triethanolamine so as to produce the triethanolamine salt of the fatty acid, or other alkanolamines may be so employed. The portion of this component in the three-component additive may range from a minimum of about 50% to a maximum of about 90% by weight based on dry solids or 100% active materials.

The salts of the sulfonic acids having a carbon chain length of 12 to 24 may be represented by the following general formula:

$$RSO_3M$$

where R is an alkyl or an alkylaryl group in which the alkyl group may be branched or unbranched and saturated or unsaturated with a number of carbon atoms in the range indicated above for the fatty acid salts and M has the same meaning as described above. Optionally, anionic sulfates may be used. The proportion of this component in two- or three-component additives may vary from 0% to about 25% by weight, based on dry solids or 100% active material.

The preferred nonionic ingredient is a polyethylene glycol derivative which may be represented by the following general formula:

$$RO(CH_2\text{-}CH_2\text{-}O)_nH$$

where n is an integer ranging from about 3 to about 30 and R is selected from a group comprising hydrogen, a fatty acid ester, an alkyl or an alkylaryl group. The proportion of this component in the additive of this invention may range from about 0 to about 25% by weight, based on dry solids or 100% active material. Optionally, other nonionic components such as fatty acid amides may be used.

In summary the present invention comprises a set of three-component additives comprising up to about 25% sulfonates with 12 to 14 carbon chain length plus from about 0% to about 25% nonionic component and the remainder being a salt of a fatty acid, all on a dry solids basis, and a set of two-component additives of like proportions except that the sulfonic acid salt is absent. In either case the additive is incorporated into a cementitious mix from about .002% to about .06% based on dry solids or 100% active ingredients with respect to total cementitious material. The two-component subsystem obtained when the nonionic component is absent is also useful. In this context the term cementitious material means portland cement plus pozzolanic addition, if any. The pozzolanic additions may be slag as well as fly ash.

In the practice of the present invention the additive is incorporated into hydraulic cement mixes such as portland cement concretes and mortars in amounts sufficient to yield an entrained air void system of the proper amount and quality after extended mixing in the plastic state. As a practical matter the additive is incorporated into the mix as an aqueous solution, which may be of any convenient concentration.

The additive may be incorporated into the mix as a portion of the mix water, but it may also be incorporated in any other convenient manner, including adding it to the dry mix before the water is incorporated therein.

The term aggregate is intended to include both fine aggregate, such as sand, and coarse aggregate, such as crushed stone or gravel, as in common in the art. In general for mortars, the aggregate may be sand or other fine aggregate meeting the requirements of ASTM standard C-33. The proportions of fine and coarse aggregate will vary depending upon the desired use and properties of the mortar or concrete. For most uses, although not limited thereto, the size of the fine aggregate will be within the broad range of about +4 mesh to -100 mesh U.S. Standard Sieve (ASTM C-11), while the size of the coarse aggregate will be within the broad range of 3 inches (7.6 cm) to

4 mesh. The coarse aggregate will usually be of mineral origin, such as gravel or crushed rock, but it may in some instances consist at least partially of graded metallic materials such as crushed iron borings, or it may be a manufactured aggregate, such as a slag.

For both mortars and concretes, the amount of water employed generally would be enough to effect hydraulic setting of cementitious material in the mix and to provide suitable workability in the plastic state. This would broadly range from about 20% to 60% by weight of the cementitious materials in mortars and about 25% to 70% by weight of the cementitious material in concrete mixes. The precise proportion of water will depend on the end use of the cementitious mix as well as on its composition.

For the purpose of illustrating the advantageous results obtainable by the practice of the present invention, plain concrete mixes were prepared and compared to similar mixes containing the additives of the present invention and functionally similar additives previously known. Since there are no standard test methods to demonstrate in the laboratory the loss of air or undesirable gain in air content on extended mixing of concretes containing air entraining agents, it was necessary to devise a procedure that is considered to be representative of practice in the field. The sequence of operations in this procedure are: preparation of concrete mixes with a nominal slump of 5 to 6 inches (10.2 to 12.7 cm) and an air content of $6.0 \pm 1.0\%$ by volume of the concrete. Each mix was designed for a total of 517 lbs/yd^3 (307 Kg/m^3) to 600 lb/yd^3 (356 Kg/m^3) of cementitious material with either portland cement alone or with a combination of portland cement and fly ash, with the latter substituted for 22% or greater of the cement by weight. The concrete, with an appropriate amount of water to attain the specified slump value is then mixed in a mixer of 2 cubic feet (.057 m^3) capacity at 20 revolutions per minute for 3 or 5 minutes. Next, specimens are taken for subsequent determination of parameters of the air void system after

hardening when desired and the initial air content is determined by the pressure meter method as described in ASTM standard test method C-231 and the slump value which is an index of workability is determined in accordance with ASTM standard method C-143. Next, agitation is continued at a reduced rate to simulate practice in the field wherein there are delays and variable delivery times, as is discussed in ASTM designation C-94, until about 30 minutes have elapsed. Then, slump and air content are again determined and the material is mixed for an additional 2 minutes. This process is repeated until about 1 hour after initial mixing has elapsed, at which time air content is again determined and additional water is added to restore initial slump. The concrete is mixed for 3 minutes, and air content is again determined. Thus the experiment is terminated at about 67 minutes after the beginning of initial mixing. The retempering by water addition at the final mixing period to restore desired slump follows field practice. It is the air content at this point which is vital to the concrete durability after hardening.

In Table I below are shown data, obtained as outlined above, at an ambient temperature of 72°F (22°C) and the cementitious material being portland cement only in the proportion of 517 lb/yd^3 (307 Kg/m^3), illustrating the problem of progressive air loss with extended mixing. Dosages of the air entraining additives are on a 100% solids or active basis, as weight percent to cementitious material. Initial slump was about 5 inches (12.7 cm).

TABLE I

Admixture	Vinsol Resin	Sodium Alpha Olefin Sulfonate
Admixture dosage, %	.0061	.00169
Initial Air Content, Vol.%	5.8	5.9
Air, After 1/2 hr. mixing	4.6	4.8
Air, after 1 hr. mixing	3.4	4.0
Air, after slump restored	3.3	3.5

The desired air content after slump restoration is a value close to the initial 5.8 volume percent. It is apparent that the air loss with extended mixing and use of Vinsol resin is very significant. Use of one component of the present invention, the sodium alpha olefin sulfonate, somewhat improves air retention, but still, to a lesser extent than is desired.

A combination of the foaming surfactant, sodium alpha olefin sulfonate, and a nonionic agent, in this case, the 1:1 molar reaction product of cocamide-diethanolamine, (DEA), when tested in a plastic concrete mix in the manner described above, and results were secured as shown in Table II.

TABLE II

Admixture	Vinsol Resin	Sodium Alpha Olefin Sulfonate plus Cocamide DEA in 5:1 Weight Ratio
Admixture Dosage, %	.0069	.0016
Initial Air Content, Vol.%	5.8	5.6
Air, after 1/2 hr. mixing	5.2	4.6
Air, after 1 hr. mixing	3.5	4.1
Air, after slump restored	3.3	3.7

It is apparent that the combination of foaming surfactant and the nonionic agent, as shown above, somewhat further benefits air retention, but still, not to the extent desired. However, when the soap of a low rosin tall oil fatty acid, is added to make a three-component air-entraining admixture, and similar tests are made, results are remarkable and unexpected, as shown by data in Table III below.

TABLE III

No.	Admixture	Dosage Wt.% of cementit. component	Initial Air Content Vol.%	Air, w/ 30 min. mixing Vol.%	Air w/ 60 min. mixing Vol.%	Air after slump restor. Vol.%
1.	Vinsol Resin	.0071	5.6	4.0	2.8	2.5
2.	AOS(1)+CD(2)+ FA(3) Wt.Ratio: 1:1/2:6-1/4	.0070	6.0	7.5	6.8	6.6
3.	AOS+CD+FA, Wt. ratio: 1:1:6-1/4	.0075	6.0	7.8	6.0	6.8
4.	AOS+CD+FA, Wt.Ratio: 1:2:6-1/4	.00685	6.0	8.0	7.1	7.0

(1) Alpha olefin sulfonate, sodium salt.

(2) cocamide-diethanolamine reaction product, described above.

(3) the tall oil fatty acid soap, described above.

The very beneficial results illustrated in Table III were unexpected and were shown by further experiments to be due to a synergistic interaction of the three components of the air-entraining agents as shown below, in Tables IV, V, and VI. In this case, the experimental conditions described above were employed except that instead of whole concrete, a mortar simulating the mortar fraction of corresponding whole concrete was employed. That is, since air entrainment occurs wholly within the mortar fraction, removal of aggregate accentuates the effects being measured.

The shorthand symbols defined above are shown in the tables and have the same meaning except that the cocamide-diethanolamine (DEA) reaction product is derived from a 1:2 molar ratio of reactants instead of a 1:1 molar ratio. It is still properly designated a cocamide DEA product, however.

TABLE IV

No.	Admixture	Dose, Wt. % of Cement	Initially Entrained air, Vol. %
1.	FA	.01	2
2.	AOS	.0016	2
3.	CD	.0032	2
4.	No. 1+No.2+No.3	.0148	14

Since 14 is significantly greater than 2 plus 2 plus 2, synergism is strongly indicatted by data in Table IV. Note that component CD, although used at twice the dosage of AOS entrains only equal air.

TABLE V

No.	Admixture	Dose, Wt. % of Cement	Initially Entrained air, Vol. %
1.	AOS	.0023	4
2.	CD	.0046	4
3.	No.1+No.2	.0069	14

Since 14 is significantly greater than 4 plus 4, data in Table V indicate a synergistic interaction in this two-component subsystem, with respect to air-entraining efficiency. Note that again the CD component must be employed at twice the dosage of the AOS component to entrain the same amount of air.

TABLE VI

No.	Admixture	Dose, Wt. % of Cement	Initially Entrained air, Vol. %
1.	FA	.0170	3
2.	CD	.0054	5
3.	No.1+No.2	.0224	14

Since 14 is significantly greater than 3 plus 5, data of Table VI indicate a synergistic interaction of the FA and CD components, with respect to air-entraining efficiency.

Further experimentation revealed that in this type of three-component air-entraining admixture, namely, a combination of a fatty acid soap, a foaming detergent and a nonionic agent as described above, that another type of nonionic agent of the class of which polyethylene glycol is an example, function in the same manner. Experiments were conducted as shown below in Table VII, employing a polyethylene glycol with an average molecular weight of 400. The experimental conditions were the same as previously described except that more severe conditions were imposed. Cement was replaced in the concrete mix by 22% of its weight with a fly ash that normally aggravates air loss on prolonged mixing of the plastic mix. The total cementitious component, that is, cement plus fly ash, was 517 lb/yd^3 (307 kg/m^3). In Table VII, the polyethylene glycol is designated PEG and the other two components are designated AOS and FA, as previously defined.

TABLE VII

No.	Admixture	Dosage Wt.% of cementit. component	Initial Air Content Vol.%	Air, w/ 30 min. mixing Vol.%	Air w/ 60 min. mixing Vol.%	Air after slump restor. Vol.%
1.	FA+PEG+AOS Wt.Ratio: .75:.125:.125	.0335	6.1	6.7	7.0	6.6
2.	FA+AOS Wt.Ratio: .86:.17	.0269	5.9	6.4	6.2	5.2
3.	FA+AOS+CD Wt. Ratio: .75:.125:.125	.0285	6.3	6.7	6.7	5.8

Data in Table VII show, in comparing Mix No. 1 and Mix No. 3, that the polyethylene glycol may be substituted for the

cocamide-diethanolamine adduct in three-component mixes, with the same component ratios and essentially the same total dosage, namely about .03 weight percent of cementitious material, and similar beneficial effects of retainment of entrained air are secured. Omission of the nonionic component, as shown in Mix No. 2, still results in a desirable result with use of the other two components, but not quite to the same degree.

Further experiments, conducted under the same conditions as described above to secure data for Table VII, led to results shown in Table VIII below. These data give insight into why combinations of components are necessary and also show that foaming detergents other than AOS can beneficially be used. The particular one shown in Table VIII is the sodium salt of dodecyl benzene sulfonic acid, where the alkyl chain is linear, and is designated DBS. Other components are indicated by symbols defined above.

TABLE VIII

No.	Admixture	Dosage Wt.% of cementit. component	Initial Air Content Vol.%	Air, w/ 30 min. mixing Vol.%	Air w/ 60 min. mixing Vol.%	Air after slump restor. Vol.%
1.	FA+PEG+DBS wt.ratio: .75:.125:.125	.0300	6.3	6.8	7.1	6.9
2.	FA	.0503	6.0	7.4	8.1	7.3
3.	AOS	.0093	6.3	2.6	2.0	1.1

In the table above, Mix No. 1 indicate that alkylaryl sulfonate salts may advantageously be employed as the foaming detergent component of the three-component admixture. Data for Mix No. 2 indicates the disadvantages of using the fatty acid salt or soap component alone, namely that a high dosage is required to secure the initial air content desired, namely about 6 volume percent, and that there is a tendency to gain air with increased mixing. Data for Mix No. 3 show the disadvantages of

employing the foaming surfactant type of air entraining agent alone, namely, that while it readily entrains the initially desired air content with a low dosage rate, it quickly loses this air with continued mixing.

The high foaming anionic detergent described above and illustrated by alkanolamine and alkali salts of sulfonic acids may be replaced by functionally similar alcohol sulfates and ethoxylated alcohol sulfates as illustrated by data in Table IX below. In this case DBS as defined above is replaced by sodium laureth 12 sulfate, designated LS. The other symbols have the same meaning earlier described. In addition the nonionic component may be ethoxylated alkylphenol, shown in Table IX as EAP. The same conditions as previously described for the fly-ash containing mixes were employed.

TABLE IX

No.	Admixture	Dosage Wt.% of cementit. component	Initial Air Content Vol.%	Air, w/ 30 min. mixing Vol.%	Air w/ 60 min. mixing Vol.%	Air after slump restor. Vol.%
1.	FA+PEG+LS Wt. Ratio .75:.125:.125	.0205	5.7	6.3	6.4	5.2
2.	FA+EAP+AOS Wt. Ratio .75:.125:.125	.0138	6.0	6.1	5.8	6.0

While the invention has been described with reference to certain preferred embodiments thereof, those skilled in the art will appreciate that various modifications and substitutions can be made without departing from the spirit of the invention. In particular in the context of this invention aqueous solutions of the components described may have added thereto small amounts of compatible chelating agents for alkaline earth cations such as magnesium or calcium which normally occur in ordinary water but which would tend to precipitate the surface active agents herein

described. Also, small amounts of compatible cosmetic coloring agents may be added. It is intended that the invention will be limited only by the scope of the claims which follow:

I claim:

1. A hydraulic cement mix comprising a hydraulic cement, aggregate in an amount of up to 80% by weight based on the total weight of said hydraulic cement mix, sufficient water to effect hydraulic setting of said hydraulic cement, and an additive comprising: mixtures of the alkanolamine and alkali metal salts of foaming detergents such as alpha olefin sulfonates alkylarylsulfonates alcohol sulfates and ethoxylated alcohol sulfates and a fatty acid soap comprising the alkali metal salts of fatty acids of the type found in tall oils; and a nonionic component selected from polyethylene glycol derivatives and the diethanolamine adducts of fatty acid amides such as cocamide, wherein the relative proportions of these three components on a 100% active basis being, respectively, ranging from 0 to 25% for the detergent, 0 to 25% for the nonionic component and 50 to 95% for the fatty acid soap and the total dosage of the combinations required to secure the desired initial air content of said cementitious system, being about 5 $\pm$ 1% by volume, and in the range of about .002 to .06 weight percent with respect to the cementitious component on a 100% active basis.

2. A hydraulic cement mix in accordance which claim 1 wherein said hydraulic cement comprises portland cement.

3. A hydraulic cement mix in accordance with claim 1 wherein said component may be a mixture of portland cement and pozzolan such as fly ash.

4. A hydraulic cement mix in accordance with claim 1 wherein said foaming detergent is the sodium salt of alpha olefin sulfonic acid.

5. A hydraulic cement mix in accordance with claim 1 wherein said foaming detergent is the sodium salt of dodecylbenzene sulfonic acid.

6. A hydraulic cement mix in accordance with claim 1 wherein said nonionic component is polyethylene glycol with an average molecular weight of about 400.

7. A process for entraining a stable air void system in hydraulic cement mixes which include the steps of preparing a mix containing hydraulic cement, aggregate in an amount up to 80% by weight, based upon the total weight of said hydraulic cement mix, and sufficient water to effect hydraulic setting of the said hydraulic cement, comprising incorporating therein an additive comprising a mixture of an alkali or alkanolamine salt of a fatty acid and a foaming detergent selected from alkali and alkanolamine salts of alkylarylsulfonic acid and alpha olefin sulfonic acid, and a nonionic component selected from polyethyleneglycol derivatives and diethanolamine adducts of cocamide, said additive being employed at the dosage required to entrain the desired level of air in said hydraulic cement mix and of itself comprising 50 to 95% by weight of the fatty acid salt and 0 to 25% of the foaming detergent and 0 to 25% of the nonionic component.

8. A process in accordance with claim 7 wherein said hyraulic cement is portland cement.

9. A process in accordance with claim 7 wherein said hydraulic component is a mixture of portland cement and fly ash.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 84/01292

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC[4] : C 04 B 28/04; 24/12 // (C 04 B 28/04; 18/08; 24/08; 24/16; 24/32) (C 04 B 28/04; 18/08; 24/12; 24/16; 24/32) ./.

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
IPC[4]	C 04 B 28/00; C 04 B 24/00

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

\-

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
X	US, A, 4375987 (B.A. LANGE et al.) 8 March 1983 see column 2, lines 27-50 and column 3, lines 6-15	1,2,7,8
X	FR, A, 2120541 (ESSO RES. & ENG.) 18 August 1972 see claims 1 and 4	7,8
X	AU, A, 521435 (ICI AUSTRALIE) 1 April 1982 see claim 7; page 12, lines 24-28	7,8
A	US, A, 3642506 (K.L. JOHNSON) 15 February 1972 see claims 1 and 15	7,8
A	DE, A, 2310810 (F.W. BRÖKER) 12 September 1974 see claim 1	6
A	Chemical Abstracts, volume 90, no. 14, issued 2 April 1979, Columbus, Ohio (US) see page 317, ref.108916a,	

./.

* Special categories of cited documents: [15]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
14 November 1984	04 JAN. 1985
International Searching Authority [1]	**Signature of Authorized Officer [20]**
EUROPEAN PATENT OFFICE	G.L.M. Kruydenberg

Form PCT/ISA/210 (second sheet) (October 1981)

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 84/01292 -2-

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC^4 : (C 04 B 28/04; 18/08; 24/08 ; 24/12; 24/16)

II. FIELDS SEARCHED

Minimum Documentation Searched [4]	
Classification System	Classification Symbols
IPC^4	

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

-

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
	& JP, A, 78132030 (SANYO CHEMICAL INDUSTRIES LTD. IWATA FUJIO) 17 November 1978	
	--	
A	A. JARRIGE: "Les Cendres Volantes", published 1971 by Editions Eyrolles, Paris (FR) see page 10 Content Survey "Use of Fly ash in concrete"	
	------------	

* Special categories of cited documents: [15]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
14th November 1984	
International Searching Authority [1]	**Signature of Authorized Officer [20]**
EUROPEAN PATENT OFFICE	G.L.M. Kruydenberg

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/US 84/01292 (SA 7730)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 27/12/84

The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A- 4375987	08/03/83	JP-A-	58099155	13/06/83
		AU-A-	9000482	02/06/83
FR-A- 2120541	18/08/72	DE-A-	2200743	20/07/72
		GB-A-	1360479	17/07/74
AU-A- 521435	01/04/82	GB-A,B	2001328	31/01/79
		FR-A-	2395969	26/01/79
		DE-A-	2829086	11/01/79
		JP-A-	54039435	26/03/79
		US-A-	4190456	26/02/80
		AU-A-	3721878	20/12/79
		CA-A-	1117150	26/01/82
US-A- 3642506	15/02/72	None		
DE-A- 2310810	12/09/74	None		

For more details about this annex :
see Official Journal of the European Patent Office, No. 12/82

This Page is Inserted by IFW Indexing and Scanning Operations and is not part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☑ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☑ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: ____________________

IMAGES ARE BEST AVAILABLE COPY.
As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.